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(54) Masterbatch resin composition for coloring.

(57) A masterbatch resin composition for coloring containing 30 to 95 wt. % of ethylene-ethyl acrylate copolymer resin having more than 7 wt. % of ethyl acrylate unit portion and more than 3 g/10 minutes of melt index and the remainder composed of one or more members selected from light-shielding materials, coloring pigments and dyes and additives.

The masterbatch resin composition of the invention is easily kneaded and extruded by extruder, and every component of the resin composition is homogeneously mixed by the extruder. Moreover, the masterbatch is easily weighed because of not scattering, and mixed with main resin. The masterbatch is suitable for automatic machines, and automatic weighing, feeding and mixing are carried out without troubles such as clogging and uneven transportation. Particularly, one masterbatch composed of the resin composition of the invention can be blended with most of polyolefin main resins. The molded products including containers and films have uniform color, and the lamp does not remain.

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MASTERBATCH RESIN COMPOSITION FOR COLORING

BACKGROUND OF THE INVENTION

Field of the Invention

Various light-shielding packaging materials for photographic photosensitive materials and colored packaging materials for magnetic materials are composed of a polyolefin resin or a composition thereof containing a light-shielding material or a coloring pigment or dye. The polyolefin resin employed is polyethylene resin, polypropylene resin, polystyrene resin or the like. Such light-shielding packaging materials for photographic photosensitive materials include magazines, cartridges, disks, light-shielding containers for loading in a light room, containers for film cartridge, various containers for camera body and light-shielding moistureproof bags, and the colored packaging materials for magnetic materials include book cases for VTR, magnetic tape cartridges for video tape or audio tape, jackets for floppy disk, floppy disk cartridges and 8 mm video tape magazines.

The present invention relates to the masterbatch resin composition for coloring used for such packaging materials.

Description of the Prior Art

Heretofore, these packaging materials were generally colored by compound coloring method where the main resin of a polyolefin resin or a polyolefin resin composition in a state of powder, pellet or melt is mixed with a light-shielding material or a coloring pigment or dye in a state of powder or granule. The mixture is supplied to an extruder, and therein, it is melted and kneaded. The molten mixture is extruded in stand shape, and cut into pellets utilized for the molding of packaging materials. However, in particular factories necessary to keep working environment clean such as the factory producing photographic photosensitive materials, it is not easy to avoid working environment pollution by the fine powder of pigments. Accordingly, the inventor has investigated a suitable method substituting for the compound coloring method, and noticed masterbath method (Japanese Patent KOKAI No. 61-179739).

The packaging materials for photographic photosensitive materials are necessary to shield from light completely, and accordingly, a large amount of a light-shielding material such as carbon black must be blended. As a result, when the same resin as the main resin is used as masterbatch resin, various problems arose, such as the fogging of the photographic photosensitive materials because of the insufficient dispersion of the light-shielding material and inferior appearance or touch because of the lumps of the light-shielding material. The lumps also resulted in molding trouble by clogging the gate of molding machine with the lumps, scratches and indentations of packaging materials, and abrasion marks, pressure marks and scratches of photographic photosensitive materials. For example, when the mixture of 70 wt. % of polystyrene resin and 30 wt. % of carbon black was extruded in strand by an extruder, the extruder molten mixture was not uniform. As a result, it became fragile, and the strand drawn out was frequently snapped off. Besides, when carbon black masterbatch was prepared by using low density polyethylene resin usable for inflation film having a melt index of 2.4 g/10 minutes and a density of 0.923 g/cm^3 as the base resin for masterbatch, the mixing of the base resin with carbon black by extruder was not uniform. As a result it became fragile, and the strand drawn out was frequently snapped off. In order to improve mixing, a large quantity of lubricant such as a higher fatty acid or a metal salt thereof was added to the mixture, and thereby, the masterbatch containing about 30 wt. % of carbon black could be prepared. However, melting of the masterbatch pellets was still not well, and lumps appeared. Therefore, thin films could not be produced. Moreover, in the case of light-shielding moistureproof bag directly to touch photographic photosensitive materials, abrasion mark trouble, pressure mark trouble, scratch trouble and the like occurred.

SUMMARY OF THE INVENTION

An object of the invention is to provide a masterbatch resin composition for coloring capable of containing a light-shielding material or a coloring pigment or dye uniformly dispersed in a high concentration.

Another object of the invention is to provide a masterbatch resin composition for coloring of which physical strength does not remarkably lower by containing a light-shielding material or a coloring pigment or dye in a high concentration and which can be extruded in strand without snapped off.

Another object of the invention is to provide a masterbatch resin composition for coloring excellent in mixing with various polyolefin resins used as main resin.

In order to achieve such objects, the inventor has investigated, and tried to blend a particular

ethylene-ethyl acrylate copolymer resin which has not been employed for the packaging materials for photographic photosensitive materials nor the packaging materials for magnetic materials with a light-shielding material or a coloring pigment or dye. As a result, the inventor has found that this resin composition can contain a light-shielding material or a coloring pigment or dye, and that it is uniformly dispersed in the resin composition by extruder. This resin composition is mixed well with various main polyolefin resins.

Thus, the present invention provides a master-batch resin composition for coloring containing 30 to 95 wt. % of ethylene-ethyl acrylate copolymer resin having more than 7 wt. % of ethyl acrylate unit portion and more than 3 g/10 minutes of melt index and the remainder composed of one or more members selected from light-shielding materials, coloring pigments and dyes and additives.

DETAILED DESCRIPTION OF THE INVENTION

As to the polymerization ratio of each monomers of the ethylene-ethyl acrylate copolymer (EEA) resin, the portion of ethyl acrylate unit is more than 7 wt. %, usually 7 to 50 wt. %, preferably 10 to 30 wt. %, more preferably 15 to 25 wt. %. The melt index of the EEA resin is more than 3 g/10 minutes, usually 3 to 20 g/10 minutes, preferably 3 to 15 g/10 minutes. Examples of such an EEA resin include "NUC-6220", "DPDJ-6182", "NUC-6170", "MB-830" and "WN-930" (all trade names, products of Nippon Unicar Co., Ltd.)

The light-shielding materials include every material not transmitting visible and ultraviolet light. Representative light-shielding materials are carbon black, metal powder and metal fiber. Carbon black, aluminum powder and its past from which volatile components are removed are preferable for the packaging material for photographic photosensitive materials in view of light-shielding ability, quality and cost.

Carbon blacks are divided into gas black, oil furnace black, anthracene black, acetylene black, lamp black, vegetable black and animal black according to their origin. Among these, oil furnace carbon black is preferable in terms of light-shielding character, cost and improvement of properties. On the other hand, since acetylene black and Ketschen carbon black have antistatic character, they are also preferable, though they are expensive. They may be blended to the oil furnace black in order to improve its character. Suitable pH of carbon black is at 5 to 9, and suitable mean particle size is 10 to 50 mμ. Particularly, the oil furnace carbon black having pH 6 to 9 and mean particle size of 15 to 30 mμ is preferable. By using the carbon black of such pH and particle size, a packaging material having the following merits is obtained. That is, the occurrence of fogging is rare, increase or decrease of photosensitivity scarcely happens, light-shielding ability is large, and the lumps of carbon black and pinholes such as fish eye hardly generate.

The coloring pigments and dyes include iron oxide, zinc white, titanium oxide, clay, calcium carbonate, mica, barium sulfate, talc, cadmium pigments, chrome yellow and red iron oxide, etc.

The kinds of the additives are not limited, however, blending of a lubricant is preferable in order to improve the mixing of the light-shielding material or the coloring pigment or dye uniformly and to lower the friction coefficient against extruder and other processing machines.

Examples of commerical lubricants suitable for the present invention include;

Silicone lubricants; "SHINETSU SILICONE" (Shinetsu Chemical Co., Ltd.) "TORAY SILICONE" (Toray Silicone Co., Ltd.), etc.

Oleic acid amide lubricants; "ARMOSLIP-CP" (Lion Akzo Co., Ltd.), "NEWTRON" and "NEWTRON E-18" (Nippon Fine Chemical Co., Ltd.), "AMIDE-O" (Nitto Kagaku K.K.), "DIAMID O-200" and "DIAMID G-200" (Nippon Kasei Chemical Co., Ltd.), etc.

Erucic acid amide lubricants; "ALFLOW P-10" (Nippon Oil and Fats Co., Ltd.), etc.

Stearic acid amide lubricants; "ALFLOW S-10" (Nippon Oil and Fats Co., Ltd.), "NEWTRON 2" (Nippon Fine Chemical Co., Ltd.), "DIAMID 200" (Nippon Kasei chemical Co., Ltd.), etc.

Bis fatty acid amide lubricants; "BISAMIDE" (Nitto Kagaku K.K.), "DIAMID-200 BIS" (Nippon Kasei Chemical Co., Ltd.), "ARMOWAX-EBS" (Lion Akzo Co., Ltd.), etc.

Alkylamine lubricants; "ELECTROSTRIPPER TS-2" (Kao Corp.) etc.

Representative other additives usable for the resin composition are illustrated as follows:

(1) Plasticizer; phthalic acid esters, glycol ester, fatty acid esters, phosphoric acid esters, etc.

(2) Stabilizer; lead compounds, cadmium compounds, zinc compounds, alkaline earth metal compounds, organic tin compounds, etc.

(3) Antistatic agent; cation surfactants, anion surfactants, nonion surfactants, ampholytic surfactants, etc.

(4) Flame retardant; phosphoric acid esters, phosphoric acid ester halides, halides, inorganic materials, polyols containing phosphor, etc.

(5) Filller; alumina, kaolin, clay, calcium carbonate, mica, talc, titanium oxide, silica, etc.

(6) Reinforcing agent; glass lobing, metallic fiber, glass fiber, glass milled fiber, carbon fiber, etc.

(7) Blowing agent; inorganic blowing agents (ammonium carbonate, sodium hydrogen carbonate), organic blowing agents (nitroso compounds, azo compounds) etc.

(8) Vulcanizing; vulcanization accelerator, acceleration assistant, etc.

(9) Deterioration preventing agent, ultraviolet absorber, antioxidant, metal deactivator, peroxide decomposing agent, etc.

(10) Nucleating agent; organic nucleating agent, inorganic nucleating agents

(11) Coupling agent; silane compounds, titanium compounds, chromium compounds, aluminum compounds etc.

(12) Various thermoplastic resins, rubbers

The resin compound of the invention contains 30 to 95 wt. % of the aforementioned EEA resin. The remainder may be a light-shielding material or a coloring pigment or dye alone. The light-shielding material or the coloring pigment or dye may be a mixture of two or more kinds of light-shielding materials, coloring pigments, dyes or the like. Besides, one or more additives may further be added to the above light-shielding material, etc. In the case that a lubricant is blended, a suitable content is 0.01 to 2 wt. %. When the content is less than 0.01 wt. %, moldability becomes worse. Shipping character also becomes insufficient, and troubles frequently occur during processing. While, when the content is beyond 2 wt. %, the resin composition becomes sticky, and dusts adhere on it. Molding cycle is elongated because of screw slip. In the case of molding film, the thickness of film becomes uneven. However, the maximum content may be raised to about 10 wt. % in the case of higher fatty acid lubricants such as oleic acid lubricants and stearic acid lubricants. The MI of the masterbatch resin composition is preferably higher than the main resin. The masterbatch resin composition for coloring of the invention is used for coloring of main resin, and the color concentration of the resin composition is higher than three times or more of the final object concentration in order to avoid the change in properties of the main resin and the decrease coloring cost.

The resin composition of the invention may be produced by mixing using a single-shaft or double-shaft extruder, a heating roller or a banbury mixer. Instead, prescribed additives such as the light-shielding material, the coloring pigment or dye, other additives or modifiers may be mixed into the solution of the EEA resin, and then the solvent is evaporated.

At the time of producing the resin composition of the invention, less than 40 wt. % of another polyolefin resin may be added to it. Particularly, when a part of main resin is previously blended into the masterbatch resin composition, the blending ability to main resin or the dispersibility of the masterbatch resin composition may be improved. On the other hand, the EEA resin granules having different sizes or two or more kinds of the EEA resin may be used for raising the extrusion rate of the masterbatch resin composition.

The main resins suitable for blending with the masterbatch resin composition of the invention include low density polyethylene resin, medium density polyethylene resin, high density polyethylene resin, linear low density polyethylene resin, ethylene-propylene copolymer resin (random type or block type), ethylene-(butene-1) copolymer resin, propylene-(butene-1) copolymer resin, ethylene-propylene-(butene-1) copolymer resin, poly(butene-1) resin, polystyrene resin, poly(methyl methacrylate) resin, styrene-acrylonitrile copolymer resin, ABS resin, polypropylene resin, crystalline propylene-α-olefin copolymer resin, modified polypropylene resin, modified polyethylene resin, polypropylene-maleic anhydride graft copolymer resin, chlorinated polyolefin resin such as chlorinated high density polyethylene resin, chlorinated low density polyethylene resin, chlorinated polyethylene copolymer resin and chlorinated atactic polypropylene resin, ethylene-vinyl acetate copolymer resin, ethylene ionomer resin (copolymer of ethylene and unsaturated acid is crosslinked by metal ion), poly(4-methylpentene-1) resin, ethylene-acrylic acid copolymer resin, ethylene-methylacrylate copolymer resin, vinyl chloride-propylene resin, ethylene-vinyl alcohol copolymer resin, crosslinked polyethylene resin (electron rays irradiation crosslinking, chemical crosslinking, etc.), polyisobutylene resin, ethylene-vinyl chloride copolymer resin and poly(1,2-butadiene) resin.

The colored resin by blended with the masterbatch resin composition of the invention is suitable for injection molding, inflation process and T die extrusion. In the case of film, it may be a single film or a coextruded multilayer film.

The masterbatch resin composition of the invention is easily kneaded and extruded by extruder, and every component of the resin composition is homogeneously mixed by the extruder. Moreover, the masterbatch is easily weighed because of not scattering, and mixed with main resin. The masterbatch is suitable for automatic machines, and automatic weighing, feeding and mixing are carried out without troubles such as clogging and uneven transportation. Particularly, one masterbatch composed of the resin composition of the invention can be blended with most of polyolefin main resins. The molded products including containers and films have uniform color, and the lump does not remain.

EXAMPLES

Product of the Invention I

68 wt. % of EEA resin ("NUC 6170", Nippon Unicar Co., Ltd., Ethyl acrylate unit content; 18 %, MI; 6 g/10 minutes, Density; 0.931 g/cm^3), 30 wt. % of oil furnance carbon black ("#44B", Mitsubishi Chemical Industries Ltd., Mean particle size; 21 mμ) and 2 wt. % of dimethylpolysiloxane ("KF-96", Shinetsu Chemical Co., Ltd.) were mixed and extruded by a double-shaft extruder ("POM 30", Ikegai Corp.) to produce coloring masterbatch pellets. 10 Parts weight of the coloring masterbatch pellets were mixed with 90 parts by weight of the pellets of high pressure branched low density polyethylene (LDPE) resin ("DFD-0111", Nippon Unicar Co., Ltd., MI; 2.4 g/10 minutes, Density; 0.923 g/cm^3), and molded into inflation film having a thickness of 50 μm by an inflation film molding machine (Placo Co., 100 mm ø ring die).

Product of the Invention II

10 parts by weight of the same coloring masterbatch pellets as used in the product of the invention I were mixed with 90 parts by weight of the pellets of low pressure linear low density polyethylene (L-LDPE) resin ("ULTZEX 2021L", Mitsui Petrochemical Industries Co., Ltd., MI; 2.1 g/10 minutes, Density; 0.922 g/cm^3), and molded into inflation film having a thickness of 50 μm by the same inflation film molding machine as above.

Conventional Product I

An inflation film having a thickness of 50 μm was prepared in the same manner as the product of the invention I, except that the same LDPE resin ("DFD-0111", Nippon Unicar Co., Ltd.) as the main resin was used as the base resin instead of the EEA resin.

Product of the Invention III

5 wt. % of the same coloring masterbatch pellets as used in the product of the invention I were mixed with 20 wt. % of the same L-LDPE resin as used in the product of the invention II and 75 wt. % of propylene-ethylene random copolymer (PP) resin ("J-950D", Mitsui Petrochemical Industries Co., Ltd., MI; 40 g/10 minutes; Density; 0.920 g/cm^3). A light-shielding tray body for loading sheet films in light room was molded by injection molding using this resin mixture.

Comparative Product I

70 wt. % of the above PP resin ("J-950D", Mitsui Petrochemical Industries Co., Ltd.) and 30 wt. % of the same carbon black as used in the product of the invention I were mixed and extruded by the same extruder as employed in the product of the invention I to produce coloring masterbatch pellets. 5 wt. % of the coloring masterbatch pellets were mixed 95 wt. % of the same PP resin ("J-950D", Mitsui Petrochemical Industries Co., Ltd.) as used in the product of the invention III, and the same tray body for loading sheet films in light room as the product of the invention III was molded by injection molding using this resin mixture.

Comparative Product II

68 wt. % of the aforementioned L-LDPE resin ("ULTZEX 2021L", Mitsui Petrochemical Industries Co., Ltd.), 30 wt. % of the same carbon black as used in the product of the invention I ("#44B", Mitsubishi Chemical Industries Ltd.) and 2 wt. % of dimethylpolysiloxane were mixed and extruded by the same extruder as employed in the product of the invention to produce coloring masterbatch pellets. 5 wt. % of the coloring masterbatch pellets were mixed with 20 wt. % of the L-LDPE resin and 75 wt. % of the PP resin, and the same tray body for loading sheet films in light room was molded by injection molding.

Product of the Invention IV

68 wt. % of the same EEA resin ("NUC 6170", Nippon Unicar Co., Ltd.), 30 wt. % of aluminum paste (Tokai Metals Co.) and 2 wt. % of stearic acid were mixed and extruded by the same extruder as employed in the product of the invention I to produce coloring masterbatch pellets. The volatile components of the above aluminum paste were previously removed up to lower than 0.1 wt. %. 10 wt. % of the coloring masterbatch pellets were mixed with 89.9 wt. % of L-LDPE resin ("MORETEC 0238N", Idemitsu Petrochemical Co., Ltd., α-olefin; octene-1, MI; 2.0 g/10 minutes, Density; 0.920 g/cm^3) and 0.1 wt. % of oleic acid amide ("ARMOSLIP CP", Lion Akzo Co., Ltd.), and molded into inflation film having a thickness of 50 μm by the same inflation film molding machine as employed in the product of the the invention I.

Product of the Invention V

98 wt. % of polystyrene resin containing synthetic rubber ("ESBRITE HH 401", Sumitomo Chemical Co., Ltd., MI; 3.7 g/10 minutes) was mixed with 2 wt. % of the carbon black coloring masterbatch pellets prepared in the product of the invention I, and a spool for photographic film was molded by an injection molding machine (Sumitomo Heavy Industries Ltd.) at mold clamping pressure of 150 t.

Product of the Invention VI

98 wt. % of polystyrene resin containing synthetic rubber ("ESBRITE NA 301", Sumitomo Chemical Co., Ltd., MI; 9 g/10 minutes) was mixed with 2 wt. % of the aluminum coloring masterbatch pellets prepared in the product of the invention IV, and a magazine for "SINGLE-EIGHT" 8 mm film (Fuji Photo Film Co., Ltd.) was molded by the same injection molding machine as employed in the product of the invention V at mold clamping pressure of 150 t.

Various properties of the above molded products were evaluated during their productions and tabulated in Table 1.

Table 1

	Invention		Conventional	Invention	Comparative		Invention		
	I	II	I	III	I	II	IV	V	VI
Molded Product	Inflation Film	"	"	Tray Body	"	"	Inflation Film	Film Spool	Film Magazine
Masterbatch Base Resin	EEA	EEA	LDPE	EEA	PP	L-LDPE	EEA	EEA	EEA
Masterbatch Light-Shielding (wt. %) Material Conc.	Carbon Black 30	"	"	"	"	"	Al Paste 30	Carbon Black 30	Al Paste 30
Main Resin	LDPE	L-LDPE	LDPE	PP L-LDPE	PP	PP L-LDPE	L-LDPE	Polystyrene	"
Light-Shielding Material Content (wt. %) of Molded Product	3	3	3	1.5	1.5	1.5	3	0.6	0.6
Blending Ability in Masterbatch	A	A	C	A	D	B	B	A	B
Blending Ability with Main Resin	A	A	C	A	D	B	B	A	B
Strength of Molded Product	B	A	D-E	A	E	A	A	B	C
Generation of Lump	A	A	C	B	C	C	A	B	A

Evaluation of Table 1 were carried out as follows:

A very excellent B excellent
C practical D having a problem
E impractical

Testing methods were as follows:

Melt Index; ASTM D-1238
Density; ASTM D-1505

Claims

1. A masterbatch resin composition for coloring containing 30 to 95 wt. % of ethylene-ethyl acrylate copolymer resin having more than 7 wt. % of ethyl acrylate unit portion and more than 3 g/10 minutes of melt index and the remainder composed of one or more members selected from light-shielding materials, coloring pigments and dyes and additives.

2. The masterbatch resin composition of claim 1 wherein said remainder is carbon black or aluminum powder.

3. The masterbatch resin composition of claim 1 wherein said remainder is carbon black or aluminum powder and a lubricant.

4. The masterbatch resin composition of claim 1 which is blended with a polyolefin main resin having a melt index lower than said masterbatch resin composition.

5. The masterbatch resin composition of claim 1 which is blended with a polyolefin resin and used for the packaging material for photographic photosensitive materials or magnetic materials.